Fuel Cell Energy Generators

PLATINUM CATALYSTS USED IN ALTERNATIVE ENERGY SOURCE

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Improvements in the preparation and utilisation of platinum metal catalysts have now made megawatt scale fuel cell systems economically viable. The high thermal efficiency and low pollution characteristics of this novel power source are likely to result in it forming an increasing proportion of the generating capacity utilised for both peaking and intermediate applications. This paper briefly reviews the development of fuel cells; it also describes how they work, including the function of the catalyst, and indicates the more important of the many factors which have to be considered when selecting a commercial system.

Fuel cells have already achieved acceptance as reliable, lightweight power sources for space applications, for example in the Apollo and Gemini projects (1).

Considerable experience has also been obtained in operating terrestrial plants to power residential, industrial and office buildings, under the TARGET programme in the United States of America. Currently in the U.S.A., commercially viable, multi-megawatt generator systems are under construction. It is now likely that fuel cells, which combine high thermal efficiency with low environmental pollution, will take a substantial share of future generating capacity. By this means the ability of the power generating utilities to respond to changing power demands will be increased, and this will help to conserve supplies of fossil fuels (2).

Most electrical energy used today is generated by alternators driven by steam turbines. The steam, in turn, is produced by burning fossil fuels (coal or hydrocarbons), or by nuclear fission. Unfortunately, the processes of converting fuel into heat, heat into steam, and steam into electricity involve efficiency losses at every stage. The Carnot cycle shows that the thermal efficiency of any heat engine is limited to $E$ where:

$$E = \frac{T_2 - T_1}{T_2}$$

$T_2$ and $T_1$ being the temperatures, in degrees kelvin, at which heat is supplied to, and rejected by, the system. In practice, upper temperatures are limited to about 500°C (773 K), lower temperatures are at least 30°C (303 K), and efficiencies are limited to a maximum of 60 per cent. Indeed most modern large power stations are able to achieve only 38 to 40 per cent efficiency.

Fuel cells convert fuel directly into electrical energy by an electrochemical route which is not limited by the Carnot cycle. Because their efficiency is not related to size, cells being developed range from 1 to 2 kilowatts to several megawatts. In contrast to batteries, the cells generate power rather than store it, and continue to do so as long as a fuel supply is maintained; there is no recharging cycle.

The simplest fuel cells run on hydrogen and oxygen; their operation is the converse of the electrolysis of water. This effect was discovered in 1839 by Sir William Grove (3), who found that electrolysis between platinum electrodes could be reversed, with the consequent generation of electric current and the production of water.

The simple unit cell, Figure 1, consists of two electrodes, one of which is supplied with hydrogen (the anode), the other with oxygen.

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These electrodes are made electrically conducting, and porous so that gases can diffuse through them. Between the electrode pair is an electrolyte, usually a strong acid or alkali. The purpose of this is to prevent mixing of the molecular gases fed to the electrodes, while permitting charged chemical species (ions) to pass from one electrode to the other carrying an electrical current. Connecting an external load across the electrodes completes a circuit, the passage of electrons through the load resistance constituting the work done by the cell.

The overall chemical reaction for this process is:

$$2H_2 + O_2 \rightarrow 2H_2O$$

In an acid electrolyte cell, the hydrogen and oxygen electrode reactions are respectively:

$$2H_2 \rightarrow 4H^+ + 4e'$$ (at the anode)

$$O_2 + 4H^+ + 4e' \rightarrow 2H_2O$$ (at the cathode)

Current is carried through the electrolyte between the electrodes by the positively charged protons ($H^+$) and round the external load by the electrons ($e'$).

Considering the thermodynamics of the system for a cell with no current flowing, that is, at reversible equilibrium; it may be shown that the standard free energy change ($\Delta G^\circ$) is related to the standard electromotive force ($E^\circ$) by the relationship:

$$\Delta G^\circ = -nFE^\circ$$

where $n$ is the number of electrons involved, and $F$ is the Faraday constant of 96,500 coulombs per equivalent. The standard free energy change for the chemical reaction forming water is $-113.38$ kcal/mol of oxygen consumed, $n=4$, and 1 calorie is 4.18 joules. The standard thermodynamic reversible potential for the hydrogen-oxygen fuel cell at $25^\circ C$ is therefore 1.229 volts.

In practice, this reversible potential is rarely attained, due to the presence of trace impurities and side reactions such as peroxide formation, mainly at the oxygen electrode (4).

The Role of the Catalyst

If a piece of inert metal ($M$) is immersed in acid and covered by hydrogen gas bubbles, some of the hydrogen molecules dissolve in the acid under equilibrium conditions. At the metal surface, some of these dissolved hydrogen molecules attach themselves loosely to the metal by donating electrons from their valency, or bonding, orbitals. A number of these atoms then become detached, leaving an electron in the metal, and exist in the solution as positively charged ions ($H^+$):

$$\frac{1}{2}H_2(gas) \rightleftharpoons \frac{1}{2}H_2(dissolved)$$

$$\frac{1}{2}H_2(dissolved) + (M) \rightleftharpoons (M)-H \rightleftharpoons M + H^+ + e'$$

The process is reversible, the exchange of electrons ($e'$) constituting a current flowing into and out of the metal. Under equilibrium conditions, the rate at which electrons are
discharged at the metal surface equals the rate at which they are released back into the electrolyte. This rate is termed the exchange current density. When a current flows to or from the electrode to an external source, the rates of reaction become unbalanced. The change in electrode potential required to achieve this inequality is termed the overpotential.

The highest exchange current densities, about $10^{-8}$ A/cm$^2$, are obtained with the platinum group metals, where hydrogen is weakly adsorbed on the metal surface, enabling a rapid formation and breaking of metal-hydrogen bonds. For metals having a high positive heat of adsorption, such as mercury, lead, tellurium, zinc and cadmium, the metal-hydrogen bond is very weak compared with the hydrogen-hydrogen bond of the molecules. Only a small proportion of the molecules have sufficient energy to dissociate and bond to the metal and the exchange current is correspondingly low ($10^{-12}$ A/cm$^2$).

With metals to which hydrogen is strongly bonded, such as molybdenum, tantalum and tungsten, hydrogen is so firmly adsorbed that further reaction is restricted, and the exchange current is again low ($10^{-9}$ A/cm$^2$). It should be noted that the exchange currents quoted are for real area of metal surface. Due to roughness factors, these may be several orders of magnitude higher than geometric areas.

Noble metal catalysts are particularly effective in fuel cells due to their high exchange current densities, and resistance to oxidation and dissolution under operating conditions.

It may be shown that as an electrode is moved away from equilibrium conditions by the application of an external current, metals with high exchange current densities exhibit lower overpotentials than metals with low exchange current densities.

Since the magnitude of the overpotential represents a voltage—and therefore efficiency—loss, and operating cells have to conduct high currents in order to do useful work, clearly it is desirable to limit overpotential and other voltage losses as far as possible. To achieve this, exchange current densities can be increased by increasing reactant concentrations, pressures and temperatures. In addition, the most catalytically active metal available should be used for the reaction, and the active surface area of the catalyst should be as large as possible.

Although the relatively simple hydrogen ionisation reaction has been used as an example of the function of the catalyst, many reactions proceed via a series of intermediate steps involving a variety of chemical species. Any one of these steps may be slower than the others, and the rate of the reaction will be governed by this slowest step. In such a situation the function of the catalyst may be to increase the rate of this limiting step so that the overall reaction will proceed much faster; although again it may well be limited by another step in the process.

**Electrode Operation**

Fuel cell electrodes perform a number of functions simultaneously. In addition to supporting the catalyst and carrying current, they must act as a barrier to prevent electrolyte escape into the gas compartment, and provide maximum area of interface between reactant gases, electrolyte, and catalyst surface.

The structure is therefore made porous to allow gas to diffuse to the reaction sites, with only a thin film of electrolyte covering the catalyst. Gases can then dissolve and diffuse rapidly to the sites during cell operation. This electrolyte/gas/solid three-phase interface may be established by incorporating a wetproofing agent, such as polytetrafluoroethylene, into the structure, Figure 2. Alternatively, the pore size distribution may be varied through the thickness of the electrode; in which case the position of the electrolyte interface is maintained by balancing capillary forces with a pressure difference across the two electrode faces.

The effect of drawing current from a fuel
cell is illustrated in Figure 3. At the oxygen electrode, region AB represents voltage losses at low currents due to activation overpotential caused by the slowness of one or more intermediate steps in the electrode reaction. Region BC is normally quite linear, and results from ohmic resistive losses in the electrode and electrolyte. A voltage gradient is necessary both to drive charged ions through the electrolyte and electrons through the electrode material.

The thickness of the electrolyte layer is normally the minimum required to prevent gas crossing from one electrode to another. A thin porous barrier of inert electrically insulating material may also be interposed between the electrodes to assist in this function, and to prevent electrodes shorting together.

The region CD represents a voltage drop caused by poor mass transport of reactants. At high current densities the gases fail to diffuse through the electrodes and pass to the reaction sites sufficiently quickly to maintain the reaction. Most activation overpotential problems occur at the oxygen electrode, the hydrogen reaction being considerably faster. Electrodes operating on air also suffer from lowered oxygen partial pressures, caused by the diluting effects of nitrogen.

**Practical Fuel Cells**

To obtain useful voltages, pairs of cells are connected in series to form stacks. These are normally flat, packed back to back in a classical filter press configuration. Electrodes may be supported by channelled backing plates, which collect current and distribute gas uniformly over the electrode surfaces. Reactant supplies are normally maintained higher than stoichiometric, that is greater than is consumed in the reaction, and the excess gases carry away heat, product water and trace impurities.

Alkaline and acid cells are usually operated at temperatures between 50 and 250°C to obtain a compromise between heat removal,
electrode activity and corrosion rate. To develop commercially viable power sources, construction materials and catalyst costs must be minimised. Air is used as oxidant, and the anodes must be tolerant of impure fuels, while still maintaining an adequate lifetime. These criteria are being met in a system developed by the United Technologies Corporation which makes extensive use of carbon as a cheap, corrosion resistant and conducting material (5).

Operation on air demands the use ofacid electrolyte to avoid carbonation problems from atmospheric carbon dioxide. Phosphoric acid is used, despite its relatively low conductivity and highly corrosive properties, in preference to other acids which are mostly unstable in a fuel cell environment.

Alternative electrolytes under evaluation include halogenated sulphonic acids, such as trifluoromethanesulphonic acid monohydrate (TFMSA). Solid polymer electrolytes have also been widely used, for example in the General Electric Company's fuel cells (6).

Noble metal catalysts have now been accepted as being the best choice, although other systems, such as tungsten carbide, have also been evaluated (7-9). Effort has been concentrated on lowering costs by optimum utilisation of very low metal loadings.

Highly effective noble metal utilisation is obtained by dispersing the metal evenly on a carbon support. By this means metal areas greater than 150 m²/g of platinum can be obtained, compared with only 30 m²/g of platinum for platinum blacks. The structure also has improved mass transport properties and resistance to metal crystallite sintering during cell operation. Although loss of metal area by sintering may be partially offset by increased activity of the resulting larger crystallites, this problem is still the most crucial aspect governing the durability of the acid fuel cell (10).

Carbon monoxide is preferentially adsorbed on platinum, poisoning the catalytic sites for hydrogen oxidation. However, at higher temperatures the degree of carbon monoxide coverage is reduced, so it has proved feasible to operate fuel cells on hydrogen obtained from a reformer system, even though this contains a small percentage of carbon monoxide, providing the operating temperature is maintained at about 190°C (11).

**High Temperature Fuel Cells**

Fuel cells which operate at high temperatures can be divided into those which employ molten carbonate electrolytes and operate at about 600 to 700°C, and solid electrolyte types operated at above 1000°C.

Molten carbonate cells rely on high temperatures to enhance reaction rates and thereby decrease electrode polarisation. Carbonate mixtures, such as lithium and potassium, are used because other species such as hydroxides, chlorides, nitrates and sulphates do not give an acceptable combination of conductivity and stability in the molten state.

Most systems envisaged involve production of hydrogen from hydrocarbons or coal by an external reformer to yield hydrogen/carbon dioxide mixtures which are fed to the anode:

\[
\text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}\quad \text{(anode reaction)}
\]

\[
\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}\quad \text{(cathode reaction)}
\]

The combusted anode gas is then enriched with air and fed to the cathode where it replaces the carbonate ion in the electrolyte. Electrodes are normally porous plaques of sintered nickel or stainless steel, with silver, copper oxide or copper for oxygen reduction. For hydrogen oxidation, anodes of nickel or silverised stainless steel may be used.

Problems encountered with the system include electrolyte losses due to evaporation and leakage during operation, electrode sintering, and gas crossover. While it is relatively simple to fabricate and run a single cell, durable interconnections between multiples of cells are difficult to achieve. At present the area of three-phase interface is greatly limited by materials of construction, and this leads to poor electrode performance.
At temperatures of about 1000°C certain oxide materials exhibit solid state electrical conductivity. The most widely studied solid electrolytes are based on zirconia. This

The First Fuel Cell

The fuel cell is generally considered to be a product of mid-twentieth century technology and to be yet some distance away from attaining its full potential as a source of energy. But its origin goes back some hundred and forty years to a remarkable man, both scientist and lawyer, who not only conceived the idea by careful experimentation but actually constructed a working fuel cell in 1842.

William Robert Grove, born in Swansea in 1811, educated at Brasenose College, Oxford, and called to the Bar in 1835, spent several of the following years at home in Swansea on investigations in electrochemistry, including the invention of the Grove cell. In a postscript dated January 1839 to a letter to The Philosophical Magazine he described an experiment on “an important illustration of the combination of gases by platinum” in which a galvanometer was permanently deflected when connected with two strips of platinum covered by tubes containing oxygen and hydrogen. By 1840 he had been elected F.R.S., and had been appointed Professor of Experimental Philosophy at the London Institution in Finsbury Circus. It was from there that he addressed a further letter, dated October 29, 1842, to The Philosophical Magazine, “On a Gaseous Voltaic Battery”. This paper (Phil. Mag., 1842, 21, 417-420) describes the first practical fuel cell, employing platinum foil coated with spongy platinum produced by electrolysis of the chloride. A series of fifty pairs, constructed as shown here in Grove’s original diagram, with dilute sulphuric acid as the electrolyte, was found “to whirl round” the needle of a galvanometer, to give a painful shock to five persons joining hands, to give a brilliant spark between charcoal points, and to decompose hydrochloric acid, potassium iodide and acidulated water.

Grove concluded his short paper with a modest but pregnant thought:

“Many other notions crowd upon my mind, but I have occupied sufficient space and must leave them for the present, hoping that other experimenters will think the subject worth pursuing.”

In later years Grove had a distinguished legal career, becoming a Q.C. in 1853 and a judge in 1871. He was knighted a year later, was made a Privy Councillor in 1887, and died at the age of 85 at his house in Harley Street, London, on the first of August, 1896.
material is stable as the monoclinic form at room temperature, and is transformed into the tetragonal form at 1150°C, accompanied by a 9 per cent volume contraction. Both these structures are similar to a cubic lattice, and by the addition of other oxides in solid solution, zirconia can be stabilised to give a cubic fluorite type of structure over certain ranges of concentration. The latter does not exhibit the volume contraction and thus minimises thermal cracking. Typical stabilisers are calcium and yttrium oxides.

The fuels generally used are hydrogen and oxygen, thus:

\[ \text{H}_2 + \text{O}^\rightarrow \text{H}_2\text{O} + 2\text{e}^- \quad \text{anode reaction} \]
\[ \text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^\rightarrow \quad \text{cathode reaction} \]

In this case, oxide ions (\( \text{O}^\rightarrow \)) act as the current carrying species in the electrolyte. If the oxygen content becomes depleted during cell operation, the material may become a semiconductor, resulting in a loss of cell efficiency.

Normally, the hydrogen is produced by an external steam reformer system. At 1000°C it would be possible to decompose hydrocarbons thermally within the cell, but there is a danger of pyrolytic carbon deposition in the anode compartment.

The cells consist of porous, sintered electrodes situated on either side of thin, flat discs of the solid electrolyte. The electrolyte has to be chemically and physically stable at the operating temperature and impermeable to gases, but as thin as possible to minimise ohmic resistance. For the cathode catalyst and current collector, the only metals sufficiently resistant to oxidation are the noble metals. However, various oxides are sufficiently catalytic and conducting to perform this task. These include copper and manganese oxides, lithium doped nickel oxide, and perovskite structures such as \( \text{LaCoO}_3 \) and \( \text{PrCoO}_3 \).

For the anodes various powdered metals such as platinum, nickel, cobalt, iron, manganese, and metal oxides such as ferric and titanium oxides are suitable, together with various carbides and cermets.

Because the problems of charge transfer polarisation—that is catalysis—are not serious at high temperatures, molten carbonate and solid oxide fuel cells offer the long-term possibility of eliminating noble metal catalysts from the fuel cell. High operating temperatures also offer greater thermal efficiency (7500 Btu/kWh) than low temperature fuel cells (9300 Btu/kWh) (5). To achieve this, however, a number of very difficult problems will have to be overcome. Corrosion, electrolyte instability and electrode sintering have up to now prevented high temperature cells demonstrating reliable, long-term operation. Countering the extreme corrosion problem entails expensive construction materials, which are also difficult to fabricate and assemble.

**Methanol Cells**

Methanol is the most promising fuel for low power terrestrial applications, such as vehicle traction and portable generators. It is easily transported and stored, and is available in bulk. It can be electrochemically oxidised to carbon dioxide and water, the thermodynamically reversible potential being 1.20 volts. Commercially attractive systems have not yet been produced, but suitable platinum metal catalysts are now being developed to yield high current densities with an acceptably low polarisation. Recently, active catalysts have been made based on the platinum-tin (12, 13) and platinum-ruthenium systems (14).

Direct methanol cells, where the fuel is dissolved in the electrolyte, have improved mass transfer characteristics compared with gas diffusion electrode types. Unfortunately, methanol also diffuses to the cathode and is chemically oxidised, but this can be prevented if a semipermeable membrane is imposed between the anode and cathode.

A number of small indirect methanol cells have also been produced. In these a water-methanol mixture is reformed to hydrogen before passing into a normal hydrogen air fuel cell (15).

The first fuel cell applications for motor
vehicles are likely to be for methanol fuelled units for public utility transport. However, from power to weight, power to volume, and cost considerations, the internal combustion engine is likely to predominate for many years to come, except of course for specialised application for the military and the aerospace industry.

**Current Technology**

The United States of America has a widely dispersed population. The country also faces a rapidly dwindling supply of fossil fuels, and increasingly severe legislation against environmental pollution. It is hardly surprising therefore that development of efficient, pollution-free fuel cells is receiving support both from the electricity utilities and from the U.S. Government. Two major programmes are in progress. The first is the construction and evaluation of a 4.8 MW unit which is intended to lead to the construction of larger 27 MW stations, each sufficient for an urban locality of 20,000 people. This size was chosen as being suitable for the generating needs of 80 per cent of the municipal and rural producers in the United States. The programme is being carried out by United Technologies Corporation (U.T.C.) and nine U.S. electric utility companies, backed by the Energy Research and Development Administration (DOE) and the Electric Power Research Institute (EPRI).

In addition, the TARGET programme aims to develop on-site generators of 40 kW capacity for residential, commercial and industrial applications. TARGET consists of a number of gas supply utilities together with U.T.C.

This programme, which has now been running for over 11 years has gained considerable experience from the operation of 65 unattended 12.5 kW units during 1972 and 1973 in the U.S.A., Canada and Japan. Both the systems are based on low temperature phosphoric acid cells, running on impure hydrogen from steam reformed hydrocarbons. The system consists of reformer, powerplant, and power conditioner sections. The latter converts direct current from the powerplant into alternating current suitable for distribution to the consumer. The three components will be available in modular form to build up the required generation capacity. Conventional steam or gas turbine generators operate at severely reduced efficiency under part load conditions. Generation is normally carried out with a mixture of different types of generators of varying sizes, each operated as close as possible to full load, in order to equate capacity with load demands. Fuel cells, however, are efficient over a range of output levels from 25 per cent to 100 per cent of rated output. Lowered current flow through the cell results in decreased ohmic losses, and in fact efficiency actually increases at part load. Gas flows to the cell are automatically and rapidly regulated to balance consumption. Equally, the fuel cell can respond to sudden increases in load demand. Normally, a utility must maintain a proportion of spare generating capacity to allow for these sudden demand changes in the form of rotating alternators, or spinning reserve. This capacity, which inevitably runs at low efficiency, would be eliminated by the presence of fuel cell reserve power.

The modular construction of fuel cells and associated plant increases its mobility, and should enable adaptation of power stations to meet changing demands caused by factors such as population growth. Modular construction also increases system reliability, allowing partial shutdown for maintenance or subsystem failure while still operating at limited capacity. This high reliability factor would allow utilities to function with smaller standby reserves than are normally kept available at a few hours notice in case of plant breakdown.

**Prospects for Fuel Cell Applications**

It has been predicted (2) that in the future electric power utilities will use nuclear or fossil fuel base load generators, running continuously at full load, and optimum efficiency.
These will be supplemented by fuel cell generators capable of providing the bulk of intermediate and peaking power requirements, thus utilising their ability to operate efficiently at part load. Because of their low pollutant emissions and silent operation, these fuel cells could be located close to centres of population, eliminating a high proportion of power transmission costs. Many city centre generating plants are over 30 years old and have high atmospheric and thermal pollution characteristics. Possible options are to attempt to clean up existing plant, incurring further efficiency penalties, to eliminate the plant completely and bring in power via underground transmission lines, or build new plant on site. Fuel cells, available as relatively small units, but with efficiencies equalling large generating stations, make the third option most feasible.

Demands for replacement generating units in the period 1980 to 1985 are: baseload units 10 per cent, intermediate units 20 per cent, and peaking units 40 per cent. This forecast (16) is based on lifetimes of 50 years, 30 years and 15 years for the respective units, taking into account the age histories of present plant in the United States. This is excluding new generating capacity, for which the estimates range from 2 to 7 per cent yearly growth rate.

The degree of market penetration achieved by fuel cell generators will depend not only on costs, which are estimated to be comparable with gas turbine units, but also on a combination of imponderables such as reliability, fuel savings and power transmission cost savings. Forecasts of the number of 27 MW powerplants installed by 1985 range from 54 to 540, and by 1990, from 146 to 1460 units (16).

The first stage of the Demonstration Programme is the construction of a 4.8 MW unit, incorporating catalysts supplied by Matthey Bishop, the Johnson Matthey affiliate in the United States of America. This unit will be evaluated on-site by Consolidated Edison in New York, as the prototype of over 50 of the 27 MW units provisionally ordered by supply utilities across the U.S.A.

Some eighteen years ago, F. T. Bacon described his fuel cell as being “at about the same stage of development as Blériot’s aeroplane” (17). By analogy, we may now be witnessing the beginning of the era of civil aviation, and the evidence at present available suggests that platinum catalysts will have a major part to play in this most essential development.

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